STUDIES IN SPECTRUM ANALYSIS

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

1895

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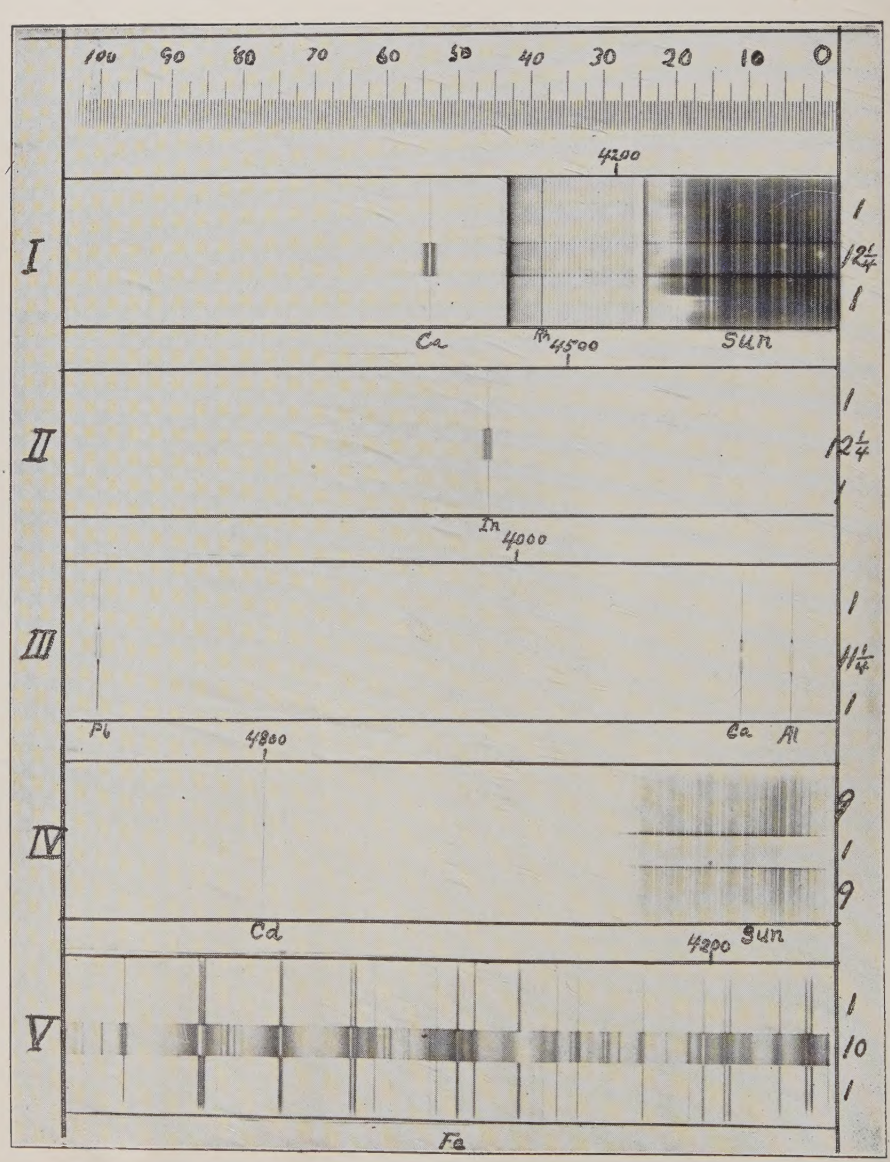
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The effect of pressure on the wave-length of lines in the spectra of the elements.

BY JOHN FRED MOHLER.

INTRODUCTION.

Kirchhoff and Bunsen,[1] as early as 1860, stated that the discontinuous spectra of gases were almost independent of the temperature and pressure at which they were produced. It would follow from this that the wave-frequency of a definite kind of light and consequently its wave-length in a definite medium is constant, or nearly so.

In the astronomical application of Doppler's principle, the constancy of the wave-length of light and also the wave-period are assumed as the basis of measurement, and the motion of the object in the line of sight is measured by the displacement of spectral lines due to the relative motion of the object and observer.

The wave-length of a definite kind of light in a definite medium has been proposed as an unchangeable and easily reproduced unit of length, and Professor Michelson[2] has measured the "Metre des Archives" in wave-lengths of cadmium light in air when the barometric pressure is 760 m. m. of mercury and the temperature is 15° Centigrade. All this work presupposes that the wave-length in a definite medium and the wave-frequency in any medium is constant.

Careful measurements of the arc and solar spectra made by Mr. L. E. Jewell in the Physical Laboratory of the Johns Hopkins University and published in Professor Rowland's[3] table of standard wave-length show certain discrepancies between the two when for very good reasons the lines are supposed to be identical, and furthermore this difference varies with different elements.

(1) Pog. An. No. 110 and 111. 1860 and 1861.

(2) Determination Experimental de la valeur du Metre en longercurs d'ondes umilnenses.

(3) Astronomy and Artro Physics.

The wave-lengths of the red, green and blue lines of the spark spectrum of cadmium vapor at low pressure as determined by Professor Michelson in the above-mentioned work differed from the values obtained by Professor Rowland for the same lines; the difference being .208 of an Angstrom unit for the red line, .173 for the green line and .186 for the blue line.

On examining spectroscopic literature it was found that many observers had noticed the fact that increase of material broadened the lines.[4] Some of the lines spread out systematically, others unsystematically, the increase in width being chiefly on the less refrangible side. Similar results have been noticed when the source of light was under pressure. In both cases the width of the line probably depends in part at least upon the vapour pressure of the element that produces it, since according to Schuster,[5] when gases are mixed in different proportions the lines of any one becomes sharper when it is present in smaller quantity, though the total pressure may remain the same.

Various theories have been proposed to explain the broadening of the spectral lines, but nowhere have we found it stated as a result of theoretical considerations or experiment that the wave-frequency itself may change and thus lead to the shift of the line as a whole. However, in speaking of absorption spectra, Kundt[6] says "The position of the absorption band of a substance depends very essentially on the dispersion of the medium in which it is dissolved or incorporated. One often observes that in a strongly dispersive media the absorption bands of a substance are displaced toward the red." It would appear from this that one might suspect the possibility of a similar phenomenon in the case of emission spectra.

APPARATUS USED.

In examining the effects of pressure on arc and spark spectra we used a twenty-one and a half foot concave Rowland grating of 20,000 lines to the inch, mounted as described by Dr. Ames in the Johns Hopkins circular of May, 1889. The arc was produced by a direct 110 volt current of from five to above fifty amperes as desired.

(4) Kayser and Runge Abh. d. k. Akd. d. W. Berlin 1890-1.
(5) Ency. Brit. article spectroscopy.
(6) Jubelband Pogg. Ann. p. 620.

For spark spectra six storage cells and a Ruhmkorff coil giving a two-inch spark were used. The pressures were obtained by pumping air into a piece of apparatus designed by Prof. Rowland several years ago for the purpose of investigating the effect of pressure on arc and spark spectra and used by Messrs. Duncan, Rowland and Todd[7] in their examination of the electric arc under pressure. It consists, as shown in the figure of a cylindrical vessel of boiler, plate A, having at each end stuffing boxes B, B^1 through which rods D, D^1 pass carrying the carbons C, C^1. The cylinder is prevented from becoming too hot by the water jacket K. A plane piece of quartz Q allows light from the arc to reach the spectroscope, and the window W enables one to adjust the carbons before turning on the current. For pressures above one atmosphere a pressure gauge was used and for low pressures a mercury manometer served to indicate the pressure in the cylinder. With low pressures the air-pump was kept working slowly during the observation and with high pressures the gauge indicated but little change after the first few seconds the arc was turned on. For a part of the work with cadmium a form of vacuum tube kindly furnished by Professor Michelson was used.[8] It was the same form that he used in his determination of the length of the "Metre des Archives" in terms of the wave-length of light. An ordinary "end on" vacuum tube was also used. It contained three centigrams of cadmium and was exhausted to 2 m. m. pressure. As the temperature to which the tube had to be raised to volatilize cadmium was nearly 300° C. this pressure was about doubled when the tube was in use. Most of the work at low pressure was done at night when the Physical Laboratory is comparatively free from vibration and when consequently one can obtain better definition than at other times. Nearly all the work was done in the second spectrum, the dispersion being a little more than one millimeter per Angstrom unit, (Rowland's scale). Some observations were taken directly with a micrometer eye piece but most of the results were obtained from photographs which were measured on a dividing engine especially constructed for this sort of work, and used in determining Rowland's table of standard wave-lengths.

(7) Electrical World, 22, 1893.
(8) Astronomy and Artrophysics, 12, 1893.

EXPERIMENTAL RESULTS.

Our first work was done with cadmium at atmospheric pressure. On varying the amount of material in the arc, the width of the lines varied accordingly, and a large amount brought out clearly the reversals of the blue and green lines. The broadening was slightly unsymmetrical, being more towards the less refrangible (red) portion of the spectrum, while the portions of the reversals coincided with those of the fine lines given by a small amount of material. Variation of strength of current did not appreciably affect the positions of the reversals of the lines of any substance examined through the width of many lines increased, that of some of them unsymmetrically with increase of current. In the case of the aluminum lines at 3944 and 3961 the red side of the reversal was much stronger than the violet side.

When pressure was applied to the arc containing cadmium, a decided *shift* in the positions of the lines was at once noticed. It was not simply unsymmetrical broadening, for it was possible to obtain fine, sharp lines with and without pressure; nor was it a case of one line disappearing and another appearing in a slightly different position, since it was often easy, while the pressure was being let off, to observe a line gradually change its position without alteration in width or other appearance. Such alterations, however, usually occurred unless special precautions were taken.

If, as is generally believed, the temperature of the arc is that of volatilizing carbon, it would be natural to suppose that it would rise with increasing pressure; but recent experiments by Wilson[1] on the temperature of the arc under pressure, seem to show that it is lower at high pressures. In either case the shift might be due to change in temperature rather than pressure, and to test this point we used a long arc perpendicular to the slit of the spectroscope. With a heavy current we exposed one part of the plate to the arc close to the positive pole and the other to the arc near the negative pole as Wilson and Gray's[2] work indicates that the temperature of the negative pole is much lower than that of the positive. We could detect no change in the position of the lines, but this of course does not settle the question, as the temperature of the electric arc and how it varies from point to point is not known. Our work

(1) Proc. R. Soc. May 30, 1895.
(2) Proc. R. Soc. Nov. 24, 1894.

would indicate that the shift of the lines was a result of change in pressure and not due to a change in temperature.

The camera of the spectroscope, which takes a nineteen by one and a quarter inch plate, is arranged for making two successive exposures, one on a narrow strip along the middle of the plate, and the other on the edges. In front of the camera, shutters were arranged to make exposures in the following order: First, to expose about one inch of the middle strip to the sun, then the remainder of the middle strip to the arc under pressure, then the corresponding outer edges to the arc at atmospheric pressure, and finally, the remaining outer edges to the sun. If plate or instrument had moved during the exposure the solar lines would show it. Besides it was noticed that the lines of the carbon bands were never appreciably shifted, and so these, some of which were found on nearly every plate, as well as the solar lines, enabled us to detect any disturbance of the apparatus during exposure.

More than one hundred and forty negatives were made, and the shifts of some lines—those that were well defined—of twenty-six[1] elements were measured in the following way: In the microscope of the dividing engine double cross-hairs were arranged giving four points of intersection at the vertices of the rhombus. As the negative was moved along by the micrometer screw, two of these intersections were used to measure the position of the lines of the middle strip and the other two to measure the position of the lines on the outer edges of the plate. The plate was then reversed and the same measurements repeated.

Let S be the shift of any line and l half the horizontal diagonal of the rhombus. Let the direct reading of the top and bottom vertices be x and the reversed reading be d, then the reading of the other vertices will be $x-l\pm s$ and $x+l\pm s$ for direct reading and $d-l\pm s$ and $d+l\pm s$ for reversed. Evidently $x+d$ is a constant from which if the reversed reading be subtracted the remainders will be x and $x+l\pm s$. The average of the two readings so obtained will be, for the upper and lower vertices equal to x, and for the others it will be $x\pm s$. The difference of these results will give the shift. By this method the accuracy of our measurements was about three thousandths of an Angstrom unit for the best lines.

(1) Twenty more have been investigated by Dr. W. J. Humphreys, A. S. 4 IV 1896.

CADMIUM.

Particular attention was given to cadmium in the hope that the discrepancy between Professor Rowland's Table of Standard Wave-lengths and Professor Michelson's measurements made at Paris might be explained. The wave-lengths of the red, green and blue cadmium lines as given by Professor Michelson and Rowland reduced to standard pressure (760 m. m.) and 20° C. and also to vacuo are given below—

	Michelson	Rowland[1]	Difference.
Red (at 760 m. m.)	6438.472	6438.680	.208
Green "	5085.824	5086.001	.177
Blue "	4799.911	4800.097	.186
Red (in vacuo)	6440.262	6440.470	.208
Green "	5087.238	5087.415	.177
Blue "	4801.245	4801.431	.186

A redetermination of the green cadmium line in the arc compared with standard lines in the Sun at wave-lengths 5014.422, 5015.123, 5020.208, 5022.414, 5068.944, 5074.932, 5083.518, 5105.718, 5109.827 and 5110.574 gave a result of 5086.000 which agrees with the above result given by Prof. Rowland.

Now if the above difference in the values of the wave-lengths of the green cadmium line is due to the differences in the standards of length used, the other difference ought to be proportional to the wave-length, *i. e.* for the blue line it ought to be .167 and for the red line .223, making an error of +.019 in one case and —.015 in the other: such an error as would be caused by a difference of barometric pressure of one centimeter of mercury or the expansion of the standard of length by a change of one degree centigrade.

This effect of pressure on wave-length is simply due to the fact that the index of refraction of air changes with the pressure and the wave-frequency is not changed at all. The change of wave-length noted below is of an entirely different character, and indicates a change in the vibration frequency of the waves.

The effect of increasing the pressure on the arc producing the cadmium lines is to shift them toward the red end of the spectrum.

The measured shift of the green and blue lines was about .010 Angstrom unit toward the red for each additional atmosphere pressure as shown by the tables below. The effect of decreasing

(1) Tables by Rowland. Astrophysical Journal.

the pressure on the arc is to shift the lines slightly toward the violet. The amount of this shift is about the same per atmosphere as it was for higher pressure; or perhaps a little greater, so that it could be stated that within the limits of pressure tried, (from 2 m. m. pressure to 10 atmospheres) the shift of the lines varies directly with the pressure. With the arc under two or three centimeters of mercury the shift of these two lines on six different plates was .014±3 toward the violet. These values were obtained by comparing the lines produced by the arc at 2 c. m. Mercury pressure with those produced by the arc at 76.36 c. m. pressure, and also by comparing the lines from the arc at low pressure with the standard lines in the sun given above.

Mr. L. E. Jewell made one set of measurements with the eyepiece micrometer on the red cadmium line, comparing it with the solar standards at wave-lengths 6431.063, 6439.298 and 6450.029 and found the shift to be .010 Angstrom unit toward the violet when the pressure of the atmosphere was reduced to .2 c. m. of Mercury. With vacuum tubes and a spark discharge, the lines were sharp but very faint from under exposure, and not good for accurate measurement, and both tubes broke after the first heating. The plates obtained however showed that the position of the lines at 2 m. m. pressure, produced by the spark, was the same as that produced by the arc under a pressure of 2 c. m. of Mercury. Professor Michelson's method of producing the light gives a much sharper line than can be obtained by the arc.

The shift of the ultra-violet line at wave-length 3403.77, however, was much smaller than that of the three other cadmium lines referred to above. It was a good line on all the plates, and the measured shift was about .004 Angstrom unit. Other ultra violet lines that occur in the cadmium series[2] were found to have a very small shift. A difference of the same kind is found in the Magnesium lines and suggests a method for identifying lines of a series.[3]

OTHER ELEMENTS.

The negatives showed that the general effect of pressure was to broaden the lines and bring out the reversals. However this was not always the case, as it was possible to obtain with cadmium

(2) J. S. Ames Phil. Mag. (5) 30, 1890.

(3) Dr. W. J. Humphreys has since followed up this suggestion with success. A. A. Oct. 1897.

and iron, for example, lines of about the same width with and without pressure; while in the case of some elements, as platinum and osmium, the lines were often narrower at high than at low pressure.

The lines of the carbon bands were brought out more strongly by pressure and at very low pressure (2 c. m.) were hardly noticeable, but as already stated they never showed any appreciable shift. This fact furnished conclusive evidence that the shift of the other lines was not due to a disturbance of the apparatus, since they were all photographed simultaneously on the same plate, the lines of the carbon bands never being appreciably displaced, while those of the other elements were. This displacement or shift varied greatly for different elements, but in the case of any one, with a few exceptions, it was approximately proportional to the wave-length. The most conclusive evidence of this proportionality was furnished by lines of different orders of spectra that appeared on the same plate. Thus ultra-violet lines of the third order were often found on the same plate with the lines of the second order of longer wave-length, but the measured shifts of the lines of the same element were in most cases approximately the same, and since the wave-length of a line of the second order that occurs at the same place is as two to three, while the dispersion in the third order is to that in the second order as three to two, it follows that constancy of measured shift is proportional to wave-length. For the sake of comparison it was found desirable to reduce the shifts of all lines to what they would be at wave-length 4000, in the neighborhood of which much of our work was done. This reduction consisted in multiplying the measured shift of any line by the ratio of 4000 to its wave-length. The lines H and K among others, as shown in table I, shift only half as much as g and the group at wave-length 5600. That g should differ in this respect from H and K is not very surprising, since it is known to differ greatly from them in many other respects. According to Lockyer[3] it is the "longest line" of the calcium spectrum; that is it occurs at the greatest range of temperature, even at that of an ordinary flame, while H and K do not appear at temperature much below that of the electric arc.

Several attempts to get the shift of the lines of Mercury were

(3) Chemistry of the Sun.

made, but the lines first tried spread out too much to admit of accurate results. There is however a group of lines at wave-lengths 3650.31[4], 3654.94 and 3663.25 which are sharp when there is little material in the arc and are nicely reversed when more material is present. Ten plates of this region were taken with pressures varying from 2 c. m. of Mercury to six and one-quarter atmospheric pressure.

The measurement of these plates showed that within these limits the shift of these mercury lines is proportional to pressure, as given in table I. These lines are sharp and clear when a spark is passed through a vacuum tube which has been exhausted by a mercury pump. Measurements on these lines on several plates taken by Dr. J. S. Ames and also on one taken by myself give results so discordant with each other and with the results obtained with the arc that further work with this element will be necessary before it can be affirmed that the arc and spark produce lines of the same wave-length in a vacuum.

Indium gave us the largest measured shift under high pressure and several plates were taken of the Indium lines at wave-lengths 4102.000 and 4511.345 at low pressure. Measurements of these lines showed a shift of .010±4 Angstrom unit toward the violet where the pressure of the atmosphere was removed. There was one precaution, however, which it was absolutely necessary to take, which was to have the lines of about the same intensity for comparison. A heavy line at low pressure, unless it was reversed, might appear to coincide exactly with a fine line at one atmosphere pressure. In this case the unsymmetrical widening of the line was sufficient to counteract the shift due to change in pressure. This source of error was more noticeable with small pressures than with large. In general, however, the lines under low pressure were very much sharper than under heavy pressure, so that though the shift to be measured was much smaller, the accuracy of setting was greater. An attempt was made to find the shift of the compound thallium line at wave-length 5350.670, but though unsuccessful in determining the shift, it may serve to show how some compound lines may have a large *apparent* shift. The line in question is a triplet. At one atmosphere pressure with but little of the element in the arc, the violet component is much the

(4) Kayser and Runge Abh. d. k. Akad. d. W. Berlin 1891-3.

strongest and the middle line the weakest. At very low pressure the red component is the strongest and the violet component the weakest. The two thallium lines at wave-lengths 3519.342 and 3529.547 show but a small displacement with pressure.

It should be stated that in some cases the value obtained for the shifts may be due in a measure to unsymmetrical broadening; but this has certainly not led to much error since only those lines were used which could be accurately measured, that is those which were either comparatively narrow or else reversed.

DESCRIPTION OF THE TABLES AND PLOTS.

Results of the measurements are given in the first table in which the upper numbers in the line of each wave-length are the observed shifts in thousandths of an Angstrom unit, and the lower their values when reduced to wave-length 4000. The curves which are all plotted to the same scale form the averages of the table, have for abscissae the reduced shifts and for ordinates the pressures in atmospheres. The wave-lengths are taken as far as possible from Prof. Rowland's table of solar wave-lengths[1]. In some cases we used a former table[2] published in Astronomy and Astrophysics. The wave-lengths of osmium, palladium and platinum were taken from a table published by Professor Rowland and Dr. Tatnall[3]; those of bismuth, tin and silver were obtained from a table by Kayser and Runge[4]. The other pressures are given in atmospheres.

The photographic plate I will give some idea of the character of the photographs obtained. At the top of the plate is a scale of wave-lengths divided into half Angstrom units. I and II are portions of the same negative, the pressures when the outer portions and middle strips were taken being respectively one and twelve and one-quarter atmospheres. I shows a portion of the solar spectrum, part of the blue carbon band, the rhodium line at wave-length 4211 and the calcium line *g*, while II shows the indium line at wave-length 4511.

This plate from which I and II were taken shows that while the solar lines are straight and the carbon lines show no displacement

(1) Astrophysical Journal I-IV.
(2) A & A 12, 1813.
(3) Astrophysical Journal Oct. 1895.
(4) Abh. d. k. Akd. w. Berlin 1892-3

the calcium line is slightly displaced and the indium line is very decidedly shifted.

III, the outer and inner portions of which were taken when the pressures were respectively one and eleven and one-quarter atmospheres, shows the aluminum line at wave-length 3961, the calcium line *H* and the lead line at wave-length 4058. IV is from a negative showing the cadmium line at wave length 4800 and a portion of the solar spectrum. In this case the middle strip was obtained when the arc was under a pressure of one atmosphere, and the outer portions when the arc was under a pressure of nine atmospheres. V is taken from a negative that was obtained when the arc was formed between a carbon negative and an iron positive pole, the pressure when the outer portions and middle strip were taken being respectively one and ten atmospheres. This photograph shows that when the lines are close together the effect of pressure is to form a practically continuous spectrum, with only reversed lines, thus in a measure approaching the appearance of the solar spectrum.

THEORETICAL RELATIONS.

In considering the numerical values of the shifts for different elements, certain mathematical relations were discovered. It was first noticed that forming for various elements the product of the cube root of the "Atomic volume" and the coefficient of linear expansion of the substance in the solid form, certain numbers were obtained whose ratios were the same as those of the shifts for the respective elements. The atomic volume is the ratio of the atomic weight to the density for any standard temperature; and its cube root was taken because the wave-length of any series of waves produced by a body varies directly as its linear dimensions. In the table given, the atomic volume and the coefficient of expansion both refer to 40 C. and the shift is that which corresponds to wave-length 4000.

The agreement of the two sets of figures may be seen in the fifth and sixth columns of the table II. Raoul Pictet[1] has used a similar expression in his formula for deducing the melting points of the metals. He finds that the continued product of the absolute temperature of the melting point, and the linear coefficient of expan-

(1) C. R. 88. 555, 1879.

sion is constant for all the metals except bismuth. The coefficient of expansion of a substance is, in a certain way, an inverse measure of the resistance of the atom to external forces; and without implying that it is a direct temperature effect, it is not unreasonable to suppose that the coefficient of expansion multiplied by the linear dimension of the atomic volume may be proportional to the change in the wave-length of the light emitted, since this product would be the actual change in the linear dimensions of the atomic volume, if there was any change in volume. Table II shows the connection of this work with that of M. Pictet, the eighth column giving the quotient of a constant, *i. e.*, 48600 divided by the absolute temperature of the melting point. The number 48600 was taken so as to reduce his results to numbers comparable with the shift at twelve atmospheric pressure, that of iron being made to coincide with the theoretical value of $x\beta^3 v$. This table shows that the shift is about as near the "theoretical value" as the melting point, and this would indicate that the product of the shift by the absolute temperature of the melting point is, with the exception of bismuth, nearly constant or that the shift is inversely proportional to the absolute temperature of the melting point.

The work shows such close agreement between the shift and $x\beta^3 v$ that the coefficient of expansion of the metals in the solid state at 40° C. may be calculated with some degree of probability if the atomic volume is known. On the above assumption, the undetermined linear coefficients of expansion of the following elements would be:

For Manganese,	.0000173
For Chromium,	.0000165
For Calcium (g line),	.0000184
For Boron,	.0000309

In the case of calcium the calculation is based on the shift of the *g* line at wave-length 4226. The fact that *H* and *K* have a different shift from *g* seems to agree with the theory that at very high temperature some substances are disassociated.

DESCRIPTION OF TABLE II.

The column marked *W* gives the atomic weights of the elements. Under *V* is given the atomic volume at 40° C. The column *x* gives the linear coefficient of expansion and the next col-

umn marked $x\rho^{\frac{1}{3}}$ gives the product of the linear coefficient of expansion by the cube root of the atomic volume multiplied by 10^6. Under S is found the reduced shift at 12 atmospheres pressure. The column marked T gives the absolute temperature of the melting point and the next column marked $\frac{48600}{T}$ gives the quotient indicated.

As noted above, the lines of the carbon bands showed no appreciable shift with the pressures employed. Indeed in some cases they were used as "base lines" from which the shift of other lines was obtained. The single carbon line at wave-length 2478 is an exception, as its shift as measured on several plates is about .046 of an Angstrom unit at twelve atmospheres pressure. In table II the values of x in the case of carbon are, first for diamond at 40° C., and second for gas carbon at the same temperature.

TABLE I.

Element.	Wave Length.	PRESSURE IN ATMOSPHERES.																											
		0	$4\frac{1}{4}$	$4\frac{3}{4}$	$5\frac{1}{2}$	6	$6\frac{1}{4}$	7	$7\frac{1}{2}$	8	9	$9\frac{1}{4}$	$9\frac{3}{4}$	10	$10\frac{1}{4}$	$10\frac{1}{2}$	$10\frac{3}{4}$	11	$11\frac{1}{4}$	$11\frac{1}{2}$	$11\frac{3}{4}$	$12\frac{1}{4}$	$12\frac{1}{2}$	$12\frac{3}{4}$	13	$13\frac{1}{2}$	14	$14\frac{1}{2}$
				17		29											44				49			48			67	
Al.,	3944.114			17		29											45				50			49			68	
"	3961.674		17	25		26		37	36							44	40				57			52			76	
"			17	25		26		37	36							45	41				58			53			77	
			17	21		28		37	36							44	42				53			50			72	
Average for Aluminum			17	21		28		37	36							45	43				54			51			73	
														26														
Bi.,	2898.08													35														
"	2989.15													34														
														45												48		
"	3397.31																									57		
														30												48		
Average for Bismuth.														40												57		
										19	23	25																
Bo.,	2496.867									30	37	40																
"	2497.821									18	22																	
										30	35																	
										19	23	25																
Average for Boron.										30	36	40																
											20	21																
C.,	2478.661										32	33						14	20					23	15			
Ca.,	3933.825K																	14	20					23	15			
															22				30			33			17			
"	3968.625H														22				30			33			17			
						18												31						28				
"	4283.169					17												29						26				
						18												22						43				

| | | |

TABLE I. — *Continued.*

Element.	Wave Length.	PRESSURE IN ATMOSPHERES.																											
		4	4¼	4¾	5	6	6¼	7	7½	8	9	9¼	9¾	10	10¼	10½	10¾	11	11¼	11½	11¾	12	12½	12¾	13	13½	14	14½
Co.,	3395.016																					24					26	
"	3405.255												17															
"	3409.336												20														23	
"	3417.384												14														27	
"	3461.326												16									23					29	
"	4121.476																					27					34	
													18															
													21															
																			20									
																			19									
													16						20			20					27	
Average for Cobalt.													19						19			24					32	
				4														26								36		
Cr.,	3886.942			4														27								37		
						16												20				12				39		
"	3919.309					16												20				12				30		
				7														33								32		
"	3941.637			7														34								33		
				7		12		16								23		27				36				47		
"	3963.831			7		12		16								23		27				36				47		
				14		12		12					25					28								38		
"	3976.839			14		12		12					25					28								38		
				12														34								49		
"	3984.059			12														34								49		
								19																				
"	4026.318							19																				
				3		9		19										26								26	30	
"	4254.505			3		9		18										24								24	28	

| | | |

TABLE I.—*Continued.*

Element.	Wave Length.	PRESSURE IN ATMOSPHERES.																												
		0	$4\frac{1}{4}$	$4\frac{3}{4}$	$5\frac{1}{2}$	6	$6\frac{1}{4}$	7	$7\frac{1}{2}$	8	9	$9\frac{1}{4}$	$9\frac{3}{4}$	10	$10\frac{1}{4}$	$10\frac{1}{2}$	$10\frac{3}{4}$	11	$11\frac{1}{4}$	$11\frac{1}{2}$	$11\frac{3}{4}$	$12\frac{1}{4}$	$12\frac{1}{2}$	$12\frac{3}{4}$	13	$13\frac{1}{2}$	14	$14\frac{1}{2}$
Fe.,	4045.975					9												20												
"	4181.919			8		9													20											
"	4199.267																		23											
"	4207.291																		23											
"	4219.516																		25											
"	4236.112																		24											
"	4250.945																		18											
"	4271.934																		17											
"	4294.301																		18											
"	4298.195																		17											
"	4325.939																													
"	4377.984																													
"	4382.928																													
"	4383.720																													
"

| | | |

TABLE I.—*Continued.*

Element.	Wave Length.	PRESSURE IN ATMOSPHERES.																									
		0	$4\frac{1}{4}$	$4\frac{3}{4}$	$5\frac{1}{2}$	6	$6\frac{1}{1}$	7	$7\frac{1}{2}$	8	9	$9\frac{1}{4}$	$9\frac{3}{4}$	10	$10\frac{1}{4}$	$10\frac{1}{2}$	$10\frac{3}{4}$	11	$11\frac{1}{4}$	$11\frac{1}{2}$	$11\frac{3}{4}$	$12\frac{1}{4}$	$12\frac{1}{2}$	$12\frac{3}{4}$	13	$13\frac{1}{2}$	14	$14\frac{1}{2}$
Mn.,..	4061. 881																	20									
																		20									
"	4235. 298			10				22																			
				10				21																			
"	4235. 450			8				18								27	37						32			36	
				8				17								25	34						29			33	
"	4239. 890			13		21													31				48			47	
				12		20													29				45			44	
"	4257. 815			14		21		22								25	39							47		47	
				13		20		21								23	36							43		43	
"	4266. 081			14		20		22								38			40				41	40		46	
				13		19		21								35			17				38	37		43	
"	4280. 257			10				21								37	43		39				41	38		44	
				9				20								34	40		36				38	35		41	
"	4284. 223			12																							
				11																							
				11		19		19								32	34	20	37				40	35		40	
Average for Manganese.				10		18		18								30	32	20	34				38	33		38	
		—5			20		22																				
Hg., ...	3650. 31	6			22		24																				
		—5			20		22																				
"	3654. 94	6			22		24																				
		—5			20		22																				
"	3663. 25	6			22		24																				
		—5			20		22																				
Average for Mercury.		6			22		24																				
																							14				
Ni.,.....	3391. 180																						17				
																							19				

| | | |

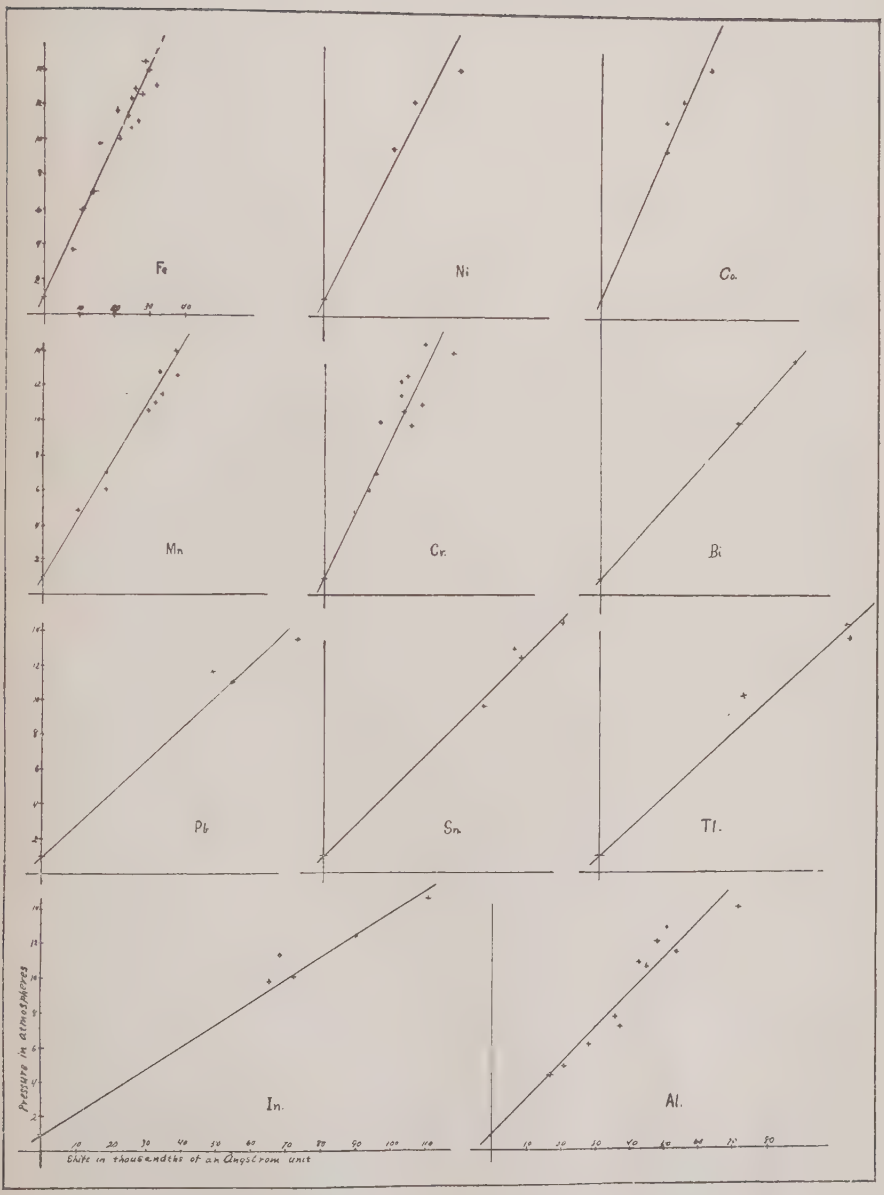
TABLE I.—*Continued.*

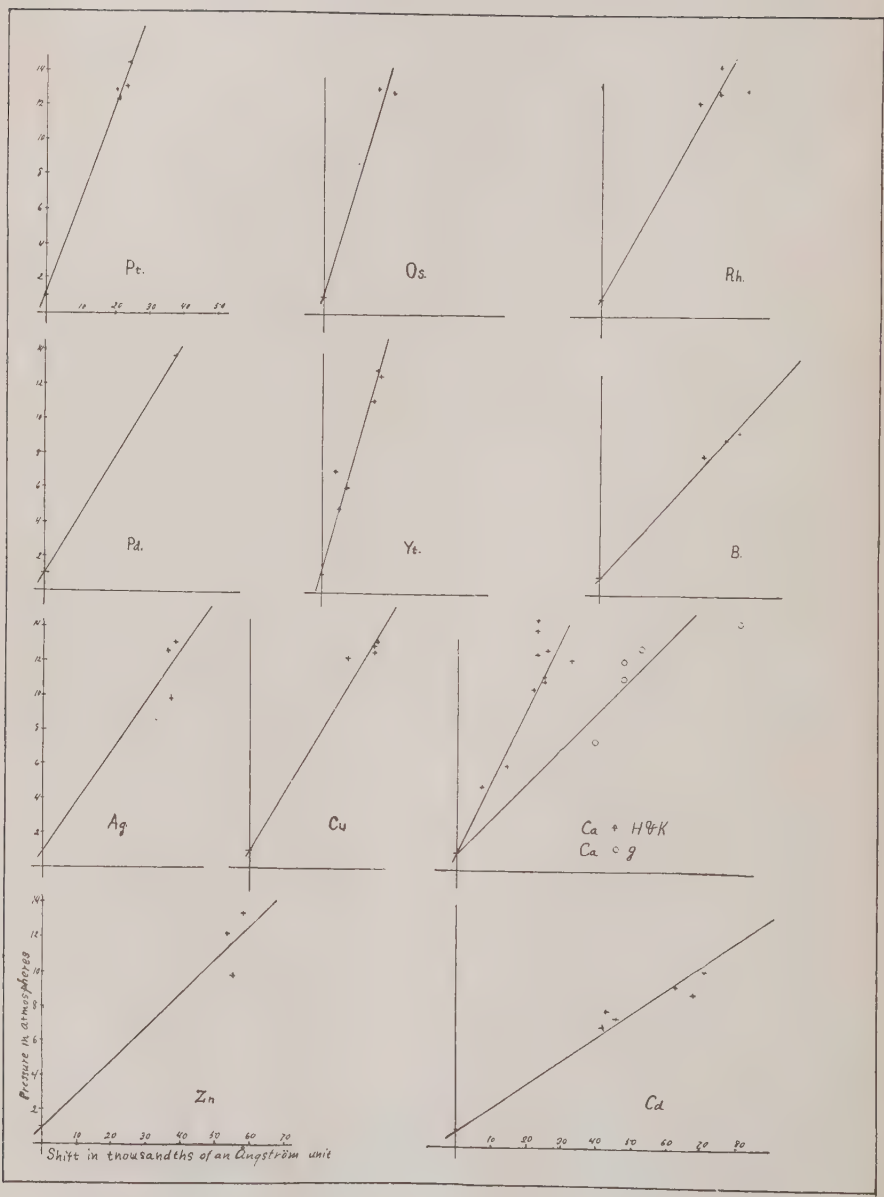
Element.	Wave Length.	PRESSURE IN ATMOSPHERES.																										
		0	4¼	4¾	5½	6	6¼	7	7½	8	9	9¼	9¾	10	10¼	10½	10¾	11	11¼	11½	11¾	12¼	12½	12¾	13	13½	14	14½
Pd.,	3460.884																									31		
"	3481.300																									25		
"	3489.915																									29		
"	3609.696																									30		
"	3634.841																									34		
"	3690.483																									44		
																										48		
																										41		
																										45		
																										28		
																										31		
																										33		
Average for Palladium.																										38		
																											45	
Rh.,	4211.6																										43	
"	4375.0																						31		38		45	37
																							28		34		41	34
																							31		38		45	37
Average for Rhodium.																							28		34		42	34
																									16			
Pt.,	2830.41																								22			
"	2893.98																								14			
"	2897.99																								20			
"	2929.91																								12			
																									17			
																								12	17			
																								16	24			

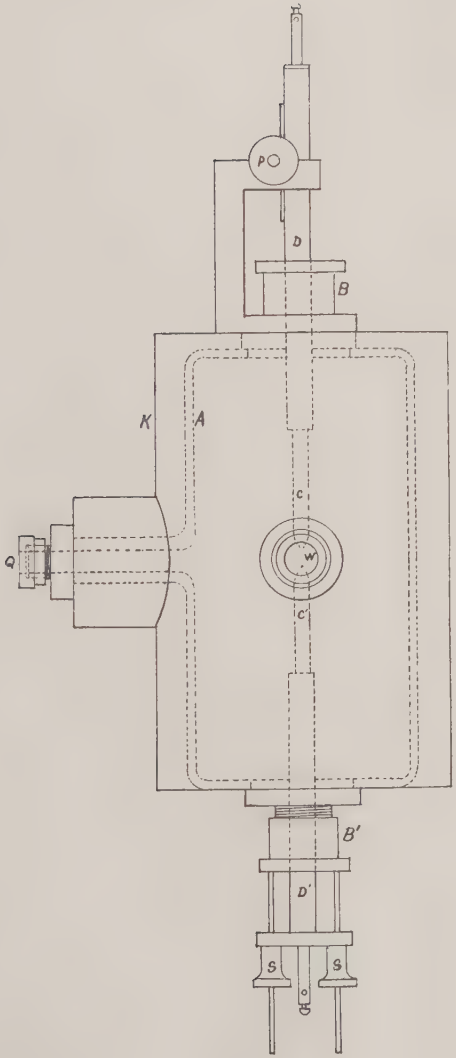
| | | |

TABLE II.

ELEMENT.	Atomic Weight. W.	Atomic Volume. V.	Lin. Coef. of Expansion. d. .0000	$d\sqrt[3]{V}$.	Shift. S.	Melting Point. T.	$\frac{48600}{T}$.
Fe., ...	55.9	7.2	.1210	23.3	25	2080	23.3
Ni., ...	58.6	6.7	.1279	24.	28	1870	26.5
Co., ...	58.6	6.9	.1236	23.6	24	2070	24.
Mn., ...	54.8	6.9			33	2170	22.9
Cr., ...	52.45	7.7			26		
Bi., ...	207.3	21.1	.1621	44.7	49	538	90.3
Pb., ...	206.4	18.1	.2924	76.9	60	605	80.3
Su., ...	118.8	16.3	.2234	58.4	55	503	96.6
Tl., ...	203.7	17.2	.3121	78.	61	563	86.3
In., ...	113.6	15.3	.4170	103.5	88	449	108.3
Al., ...	27.1	10.6	.2313	50.6	55	1123	43.3
Pt., ...	194.3	9.1	.0899	18.5	20	2050	23.7
Os., ...	190.3	8.5	.0657	13.4	17	2770	17.5
Rh., ...	104.1	8.6	.0850	17.4	30	2270	21.4
Pd., ...	106.35	9.2	.1176	24.7	33	1775	27.4
Y., ...	88.9				15		
B., ...	10.9	4.			49		
C. diamond	11.97	3.6	.0118	2.7	0		
C. graphite	11.97	3.6	.0540	8.2	0		
Ag., ...	107.7	10.2	.1921	42.2	38	1230	39.5
Cu., ...	63.18	7.1	1678	32.5	33	1330	36.5
Ca. H. & K.	39.91	25.4			27		
Ca. g., ...	39.91	25.4			54		
Zu., ...	65.10	9.1	.2918	61.2	57	676	71.9
Cd., ...	111.7	12.9	.3069	75.6	80	593	82.
Hg., ...	199.8	[14.1]			56	233	208.
Mg.	24.3	13.9			92	1023	47.


Fe
Ni
Co.
Mn
Cr.
Bi
Pb
Sn
Tl.
In.
Al.
Pressure in atmospheres
Shift in thousandths of an Ångström unit


Pt.
Os.
Rh.
Pd.
Yt.
B.
Ag
Cu
Ca + H&K
Ca g
Zn
Cd
Pressure in atmospheres
Shift in thousandths of an Ångström unit


P
D
B
K
A
C
Q
W
C'
B'
D'
S
S

THE PRESSURE OF THE "REVERSING LAYER" ON THE SOLAR ATMOSPHERE.

The investigation of the effect of pressure on the wave-lengths of the lines of the arc spectra, together with the observations made by Mr. Jewell that many lines of the solar spectrum do not quite coincide with the corresponding lines of the arc spectra at atmospheric pressure, seems to furnish a method of determining the pressures of the solar atmosphere where the Fraunhoffer lines are produced.

The difference between the wave-lengths of the lines of ordinary arc spectra and those of the sun is most marked in the case of those that are strong in the solar spectrum, and at the same time strongly reversed in the arc. Most of the lines mentioned below are of this character. Assuming that the solar atmosphere is comparatively quiescent, and that the displacements of the lines in the solar spectrum, referred to the arc at atmospheric pressure (referred to the same standard) are both due to pressure, we find, on comparing these displacements and shifts, the results shown in the following table III. It will be noticed that two pressures, corresponding to two groups of lines, are given for the reversing layer of calcium.

This comes from the difference in the shifts of these lines in the spectrum of the arc under pressure, but excepting the lines *H* and *K* and *g*, the two groups present the same appearance in the solar spectrum. The lines *H* and *K* are peculiar in many respects, and are often displaced much more than any other calcium lines. Their positions, however, relative to other solar lines are found to be different on different plates, and the difference in position is connected with certain peculiarities in appearance. Besides, they occur in the chromosphere, and always in prominences where the pressure is comparatively small. The narrowness of the central line in both *H* and *K* likewise indicates a comparatively low pressure for their final absorption. These facts, especially the difference in the positions of *H* and *K* on different plates, and their occurrence at great altitudes, make it appear probable that their displacements may be accounted for, at least in part, by motion in the line of sight.

Their general appearance seems to indicate an enormous amount of material present throughout a great range of elevation and pressure, while the appearance of *g* indicates only a small amount of material with a limited range of elevation and pressure. These observations, as may be seen from the table, seem to indicate that possibly the upper limits of the reversing layers of the different elements in the solar atmosphere are arranged somewhat in the order of their atomic weights, those of heavier atomic weight being at greater pressure, and consequently smaller elevation.

TABLE III.

Element.	Wave-length.	Pressure of "reversing layer."
Aluminum,	3944.160	2 atmospheres.
"	3961.674	
Silicon,	3905.660	4 "
Calcium,	4283.169	
"	4289.525	6 "
"	4299 149	
"	4302.692	
"	4226.904	
"	5588.985	3 "
"	5594.691	
"	5598.711	
Chromium,	Several lines	5 "
Manganese,	" "	6 "
Iron,	" "	7 "
Nickel,	" "	7 "
Copper,	" "	7 "
Cobalt,	" "	4 "

ON THE WAVE-LENGTH OF SOME OF THE HELIUM LINES IN THE VACUUM TUBE AND OF D_3 IN THE SUN.

Through the kindness of Dr. W. W. Randall and Professor Ira Remsen, Mr. L. E. Jewell and myself obtained the use of a tube filled with pure helium by Professor Ramsay, and have measured the lines produced by that tube and also the D_3 line in the sun. The same grating and dividing engine used in the work on the shift of the lines was used for this work. Several photographs were taken with iron lines in the arc for comparison lines. The comparison lines for the direct measurements were carefully selected solar lines.

As several of the ultra-violet helium lines appeared on the same photographic plates with D_3 they also were measured.

One photograph was taken in the first spectrum with an exposure of three hours, another in the second spectrum with an exposure of five hours, and a third plate was given two and a half hours' exposure in the second spectrum. All these plates were taken at night when the building was perfectly quiet and the definition is excellent, especially in the plate exposed two and one-half hours.

Table IV gives the results of measurements made on the lines produced in the vacuum tube, the first three values of the two components of D_3 being the results of measurements made with the eye-piece micrometer using solar lines for comparison. The wave-lengths of these lines are taken from the table of solar spectrum wave-lengths published in the Astrophysical Journal by Professor Rowland[1].

The remainder of table IV gives the results of the measurements of the photographic plates. The wave-lengths of the standards here used are from Mr. Jewell's[2] article in the Astrophysical Journal, February, 1896, and from Professor Rowland's table of standards. The observations marked "J" were made by Mr. Jewell and those marked "M" by myself. Table II gives the position of D in the chromosphere of the sun and also in the neighborhood

(1) Astrophysical Journal I-VI.

(2) Astrophysical Journal 3, January 1896.

of sun spots. Mr. Jewell made these measurements with a large plane grating of 15000 lines to the inch. Table III gives the mean values of our measurements and also the values given for the same lines by Runge and Paschen.

The lines produced by the vacuum tube were sharp and clear, both when viewed directly and on photographic plates, although in both cases the first component was somewhat difficult to measure. In the chromosphere the lines are diffused and broad, and the two components not easily separated; consequently the measurements on the faint component are little more than estimates. Directly over sun spots the lines were usually more faint, but near the spots, (probably over faculæ) the principal component was fairly dark and narrow, and the faint component just visible, but too faint to measure, so that the measurements were made on the principal component alone. The two lines used for standards, although small, are sharp and clear and equally distant from D_3. During the two days upon which these measurements were made the air was very dry, and the water-vapor lines in the neighborhood almost invisible. The wave-length of the principal component near sun spots is less than in the chromosphere. This might indicate an uprush of material at these places, or a lowering of pressure; this is the effect that might be expected over prominences. The difference in intensity of the two components of D_3 being so great, measurements upon it as a single line vary according as the cross-hairs of the instrument are set upon the middle of the line, or upon the position of maximum intensity, therefore the personal equation of the observer enters quite largely into such determinations of its position.

As a consequence of this the results of different observers as published vary greatly and any such determination must be necessarily unsatisfactory.

TABLE IV.

LINES PRODUCED BY A VACUUM-TUBE CONTAINING HELIUM.

Helium Wave length	Intensity	Observer	Number of readings	Spectrum	Comparison Lines
D_3 5875.813	5	J.	2	II	5853.902, 5859.809, 5862.582, 5866.675, 5893.097
D_3 5876.148	1	J.	2	II	5905.895, 5916.475, 5919.860, 5930.406, 5934.881
D_3 5875.815	5	J.	2	II	Same as above.
D_3 5876.150	1	J.	2	II	
D_3 5875.812	5	M.	2	II	5853.902, 5859.809, 5862.582, 5866.675,
D_3 5876.153	1	M.	2	II	5905.895, 5916.475, 5919.860, 5930.406.
Ghost 3888.771		M.	2	II	
3888.754	10	M.	2	II	3865.665, 3878.161, 3878.709, 3886.415, 3888.661
3888.851	2	M.	2	II	3903.087, 3905.661, 3920.398, 3923.038, 3928.059
D_3 3875.816	5	M.	2	II	3930.438, 3944.160.
D_3 5876.132	1	M.	2	II	
*3888.656	0	J.	4	II	
Ghosts 3888.771		J.	4	II	
3888.758	10	J.	4	II	3886.415, 3888.661, 3903.081, 3905.661,
3888.859	1	J.	4	II	3920.396, 3923.038, 3928.059, 3930.438.
D_3 5875.812	5	J.	4	II	
D_3 5876.151	1	J.	4	II	
D_3 5876.149	1	J.	8	II	Difference on plate exposed five hours.
D_3 5876.150	1	M.	10	II	
4026.325	3	M.	2	II	4005.399, 4030.900, 4033.213, 4034.631, 4045.964, 4063.751, 4071.896.
4026.500	0	J.	5	II	Difference on plate above.
D_3 5875.802	5	J.	2	I	2912.267, 2929.121, 2937 014, 2947.986, 2954.050
D_3 5876.146	1	J.	2	I	2957.477, 2965.373, 2970 213, 2981.558, 2983.681
D_3 5875.802	5	M.	2	I	2912.267, 2929.121, 2937.014, 2997.986,
D_3 5856.130	1	M.	2	I	2973.347, 2983.681.
D_3 5875.814	5	M.	2	I	Same as above.
D_3 5876.146	1	M.	2	I	

*It is uncertain whether this weak line belongs to helium or some impurity.

TABLE V.

POSITION OF THE D_3 LINES IN THE SOLAR SPECTRUM.

Wave-length	Intensity	Observer	Order of Spectrum	Number of readings	Position	Comparison Lines.
5875.857		J.	II	5	West limb	5873.436, 5878.015
5876.188		J.	II	4	West limb	" "
5875.824		J.	II	5	East limb	" "
5876.175		J.	II	5	East limb	" "
5875.815		J.	II	13	Near Sun-spots	" "

TABLE VI.

Mean Values for the vacuum tube Jewell and Mohler	Mean value for the chromosphere	Mean value for vicinity of Sun-spots	Values given by Runge and Paschen[1]
3888.766			3888.785
3888.855			
4026.325			4026.342
4026.500			4026.512
D_3 5875.812	D_3 5875.841		5875.870
D_3 5876.147	D_3 5876.182	D_3 5875.815	5876.209

DISTANCE BETWEEN THE COMPONENTS OF D_3.

Runge and Paschen, vacuum tube 0.339. Mohler and Jewell, vacuum tube, 0.335
Hale and Ellerman, solar prominence, 0.357.

TABLE VII.

LINES IN THE VICINITY OF D_3 IN THE SOLAR SPECTRUM.

Wave-length	Substance	Intensity
5875.330	A (wv)	0
5875.425		00000
5875.512		0000
5875.665	A (wv)	00
5875.810	A (wv)	0
5875.970	A (wv)?	000N
5876.160	A (wv)?	0000N
5876.340	A (wv)	1
5876.513		00N
5876.660	A (wv)	0
5876.775	A (wv)	000

PHYSICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
March 12, 1896.

[1]ASTROPHYSICAL JOURNAL, January, 1896.

Work was begun on the investigation of the effect of pressure on wave-lengths in February, 1895, by Dr. Humphreys and myself, and together we did the work at pressures greater than one atmosphere.

The fact that the shift in the case of any one element is proportional to wave length and that for different elements is proportional to $x\sqrt[3]{v}$ was discovered by myself.

The fact that in the case of elements of the same half of a Mendelejiff group the shift is in most cases proportional to the cube root of the atomic weight, was subsequently discovered by Dr. Humphreys as noted above. The note on the pressure of the reversing layer of the sun is joint work and connects our work with pressure with the observations of Mr. L. E. Jewell. The work on the effect of pressure when the pressure was less than one atmosphere was done by myself. The measurements of the D_3 and Helium lines was made in connection with Mr. L. E. Jewell.

A paper on the effect of pressure on the arc spectra was read by myself at the Springfield meeting of A. A. A. S. in August, 1895, and an article published in the Astrophysical Journal February, 1896.

An abstract of this paper was read before the Scientific Convention of Johns Hopkins University, January 23rd, 1896, and published in the Johns Hopkins Circular of February, 1896.

The paper on the pressure of the reversing layer of the sun was published February, 1896, in the Astrophysical Journal, and my second article on the Effect of Pressure on wave-lengths was published in the same journal October, 1896. The work on the wave-lengths of the line D_3 and helium was published May, 1896, in the Astrophysical Journal.

ACKNOWLEDGMENT.

All the work was done at the Johns Hopkins University under the direction and with the assistance of Professor Rowland and Dr. Joseph S. Ames, the directors of the Physical Laboratory. I wish here to thank these gentlemen for their kind assistance. Much of the work is due to their direct suggestion, and the pressure apparatus used was made by Professor Rowland several years ago for this purpose but laid aside for more important work. I wish to acknowledge the kindness of Professor Michelson in sending me a cadmium tube, and I am also indebted to Dr. W. W. Randall for lending me the helium tube.

BIOGRAPHICAL SKETCH.

The author was born near Carlisle, Pennsylvania, October 30, 1864, and from the age of six to sixteen attended the public schools of his native county. From 1881-1883 he taught in the public schools and at the same time prepared for College. In the Fall of 1883 he entered Dickinson College where he took the Classical Scientific course and graduated as Valedictorian of his class in 1887, receiving the degree of A. B. He was instructor in Science and Mathematics in the Wilmington Conference Academy at Dover, Delaware, from 1887-1890, and was instructor in Mathematics at Wesleyan Academy, Wilbraham, Massachusetts, from 1890-1894. In October, 1894, he entered Johns Hopkins University as a graduate student, choosing Physics as his principal subject and Astronomy and Mathematics subordinate subjects. In 1895 he was appointed Student Assistant in Astronomy and in 1896, Fellow. In June, 1896, he was elected to the chair of Physics in Dickinson College.